THERMO-MECHANICAL TREATED LEAD AND LEAD ALLOYS ESPECIALLY FOR CURRENT COLLECTORS AND CONNECTORS IN LEAD-ACID BATTERIES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a Continuation-in-Part of pending application Serial No. 09/412,610 filed October 6, 1999, which is a Continuation-in-Part of application Serial No. 08/977,518 filed November 24, 1997, which is a Continuation-in-Part of application Serial No. 08/835,926 filed April 8, 1997 (abandoned), which is a Continuation of application Serial No. 08/609,327 filed March 1, 1996 (abandoned).

FIELD OF THE INVENTION

This invention relates to wrought and recrystallized lead and lead alloys, with increased resistance to creep and intergranular cracking and corrosion. This invention is more particularly concerned with positive lead and lead alloy current collectors and connectors used in lead-acid batteries which, via recrystallization treatment to generate new grain boundaries in the microstructure, have improved resistance to corrosion and growth, so as to provide enhanced battery reliability, extended service life and greater energy density.

BACKGROUND OF THE INVENTION

Intergranular degradation (i.e., creep deformation, cracking and corrosion) of lead-based positive current collector grids, tubular spines, foils and connectors (straps, lugs, posts) are the principal cause of premature failure of lead-acid batteries. Intergranular corrosion occurs when Pb current collector and its components are transformed to PbO_2. Intergranular corrosion limits the life of automotive batteries and affects the life of industrial batteries.

5   Creep deformation, which arises primarily from grain boundary sliding processes, results in dimensional expansion of the positive current collector. The so-called "growth" causes a loss of contact between the electrode surface and the PbO_2 paste and leads to shorting between adjacent electrodes. The growth of the positive current collector also contributes to intergranular "cracking".

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       Growth of the positive current collector in lead-acid batteries is the predominant failure mode of automotive batteries as under-the-hood temperatures in modern automobiles increase. As a result of these intergranular degradation processes, and in order to maintain sufficient operating- and cycle- life performance, considerable weight allowances are required on the

15   minimum dimension of the positive current collectors, which commensurately increase the overall size and weight of the batteries.

       Early improvements in positive lead grids were obtained by alloying the lead with: Sb, Sn, As, Ca and other elements. These efforts were made to strengthen the alloys by precipitation

20   or age hardening, such as are disclosed in the United States Patent Nos. 4,753,688 to Myers, 1,675,644 to Dean and 3,888,703 to Tilman, all of which are directed to antimony-bearing lead alloys. Precipitation and age hardening techniques require the presence of an alloying element which is not soluble in lead at ambient or operating temperature, and which forms a second phase in the metal. Hardening is typically achieved by straining and then heat treating the lead alloy

25   above the solvus temperature, to solutionize the second phase, and then quenching the metal to form a supersaturated solution of the alloyed element in the lead. Over time, the alloyed element precipitates out of solution to form a second phase, preferably in the form of small precipitates, in the metal. These second phase precipitates impede dislocation motion in the metal, inhibit grain boundary sliding, and consequently strengthen and harden the material. Quenching following the

30   heat treatment is necessary to keep the precipitate size small and effective in terms of strengthening and growth resistance. The deformation prior to heat treatment, typically achieved through cold or hot working, forms dislocations in the crystallographic structure of the metal which act as the nucleation sites for the precipitation of the second phase, and result in a more uniform precipitate distribution.

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It should be noted that as a result of the relatively low melting temperature of lead and lead alloys, precipitation hardening typically occurs at room temperature. The techniques taught in the prior art, as exemplified in the above listed patents, are primarily directed to reduction of the time required to achieve optimum strength, from a few days at room temperature to a few

10 minutes at elevated furnace temperatures.

There has also been a general recognition by the lead-acid battery industry, that wrought lead-alloys which are cold worked following casting of the molten alloys, yield enhanced growth resistance relative to lead and lead alloys which are simply cast to final shape. This performance

15 improvement has been attributed to 'microstructural' refinement, and examples are outlined in US Patent Nos. 5,611,128 and 5,604,058 to Wirtz, which describe processes to cold roll near net shape battery electrodes from cast grid blanks. The benefits obtained from such wrought lead alloys may also be attributable to precipitation processes whereby uniform precipitate distribution is obtained by longer term aging at ambient temperature. In this regard, it should be noted that

20 performance improvements using 'wrought' electrodes have been observed only with lead alloys containing alloy constituents such as Ca, Sr, Sb, Ba etc.,which are insoluble at ambient temperature, and form precipitates on aging. Moreover, both precipitation-processed and wrought electrodes have not been shown to display any significant improvements with regard to intergranular corrosion.

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Precipitation hardening processes, involving the proper choice of alloying constituents, and prior deformation to enhance the uniformity of precipitate distribution from aging at ambient or elevated temperature, undoubtedly have a beneficial impact on minimizing grid growth from grain boundary sliding (i.e., grain boundary "pinning by precipitates"). We have found that it is

30 preferable to alter the structure of grain boundaries in the material directly, not only to impede grain boundary sliding, but also to minimize intergranular corrosion and cracking susceptibility. Unlike precipitation-based processes, such a new approach, according to the present invention, is also applicable to pure lead and lead alloys not containing precipitate-formers. This opens the way to the advantageous use of less expensive alloys.

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       Various studies have shown that certain special grain boundaries, described on the basis of "Coincident Site Lattice" model of interface structure (Kronberg, and Wilson. Trans. Met. Soc. AIME, 185, 501 (1949), as lying within $\Delta\theta$ of Σ, where $\Sigma \leq 29$ and $\Delta\theta \leq 15°\Sigma^{-1/2}$ (Brandon, Acta Metall., 14, 1479 (1966)) are highly resistant to intergranular degradation processes such as

10   corrosion, cracking, and grain boundary sliding; the latter being a principal contributor to creep deformation. However, these studies provide no instruction as to how to achieve a high concentration of special grain boundaries, and as noted, it is only recently that techniques such as Orientation Imaging Microscopy have become available to determine the concentration of special grain boundaries in a polycrystalline material. Moreover, the only means of creating new grain

15   boundaries during solid state processing is to effect recrystallization of a material by deformation followed by suitable heat treatment; such a novel approach to the processing of lead acid battery positive current collectors therefore forms the basis of the present invention.

       Palumbo in US Patent Nos. 5,702,543 (1997), and 5,817,193 (1998), describes a thermo-

20   mechanical process for increasing the population of such special grain boundaries in commercial austenitic Fe and Ni-based stainless alloys from approximately 20-30% to levels in excess of 60%; such an increase resulting in significantly improved resistance to intergranular degradation processes such as intergranular corrosion and stress corrosion cracking. However, the process described and claimed in these patents is directed exclusively to certain austenitic stainless steels

25   and nickel-based alloys, and not with any other metals. The intended application of such alloys and the environment they encounter in use is quite different from the harsh, acidic environment of lead-acid batteries.

       Lehockey in US Patent No. 6,086,691 (2000) discloses a thermo-mechanical process for

30   increasing the population of such special grain boundaries in commercial Pb-alloy electrowinning electrode materials to levels in excess of 50% by cold deforming a Pb-alloy sheet to achieve a thickness reduction of 30% to 80% and annealing the material at temperatures ranging from 180 °C to 300 °C for 15 to 30 minutes and repeating the deformation/annealing treatment for a second cycle

5   Rao in WO/00/60677 (2000) describes a method for making Pb-Ca-Sn-Ag grids by casting an alloy strip and then "hot rolling" the strip at a temperature between the solvus temperature and the peritectic temperature of the alloy, quenching the hot rolled strip and preferably heat aging the strip at a temperature of 200°F (93°C) to 500°F (260°C) to enhance

10   mechanical and high temperature corrosion characteristics prior to perforating the strip, e.g. by an expansion process to fabricate suitable battery grids.

          Peening is a non-conventional method of deformation in which compressive stresses are induced in the exposed surface layers of metallic parts by the impingement of a stream of shot,

15   directed at the surface at high velocities under controlled conditions. Peening cleans the surface of the test article, increases the fatigue strength and relieves tensile stresses that contribute to stress-corrosion cracking. Yamada in U.S. 5,816,088 (1998) describes a surface treatment method for a steel work piece using high speed shot peening. Mannava in U.S. 5,932,120 (1999) describes a laser shock peening apparatus using a low energy laser.

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OBJECTIVES OF THIS INVENTION

          It is an object of this invention to provide a method for making current collectors from

25   lead and lead-alloyed with at least one element selected from the group of Ag, Al, As, Ba, Bi, Ca, Cd, Cu, Li, Mg, Na, Se, Sb, Sn, Sr, and Zn utilizing gravity or continuous casting; casting a billet followed by extrusion and/or rolling, and, if desired suitably perforating the strip e.g. by expansion or punching. In its final form the current collector can be a bookmold grid, a tubular grid, a foil or sheet, a perforated strip, i.e. suitably punched or expanded, a continuous cast grid or

30   a continuous cast grid which is subsequently rolled to its final dimension.

          It is an object of this invention to provide a method for making current collectors for flooded, gelled or valve regulated lead-acid batteries by implementing the novel thermo-mechanical process into the continuous "conventional" manufacturing process.

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It is an object of this invention to provide a method for making current collectors for flooded, gelled or valve regulated lead-acid batteries by implementing the novel thermo-mechanical process after the completion of "conventional" manufacturing process by treating at least part of the outer surface of the current collector in its final or near-final shape.

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It is an object of this invention to provide a method for treating current collectors made by the "Properzi" process (Contiouus S.p.A. Milan, Italy), whereby a billet is continuously cast and thereafter rolled to the desired thickness and optionally suitably perforated using reciprocating expansion, rotary expansion or punching.

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It is an object of this invention to provide a method for bulk treating current collectors made by continuous casting grid-rawlings and using the "Con Roll" process (Wirtz Manufacturing Inc., Port Huron, Mi, USA), whereby a grid like structure is continuously cast and thereafter rolled to the desired dimension.

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It is an object of this invention to provide a method for treating current collectors made by the "Cominco" continuously drum casting process as described by Vincze in US 5,462,109, the specification of which is incorporated by reference, (Teck-Cominco Ltd, Vancouver, BC, Canada) and optionally suitably rolling the strip to the desired thickness, optionally followed by a suitable

25   perforation.

It is an object of this invention to provide a method for treating current collectors made by casting a billet and extruding a strip to the desired thickness, followed by optional rolling and optional strip perforation.

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5   It is a further object of this invention to provide a process which enables the treatment of a finished part without imparting a substantial dimensional change as is normally the case by conventional deformation operations used, including rolling, extruding, forging and the like. This feature enables the treatment of finished parts, e.g. bookmould cast lead-acid battery grids, tubular grids, Pb and Pb-alloy straps and posts as well as "Conroll" grids without substantial deformation

10   of the part.

       It is a further object of the present invention to provide a peening process, optionally followed by a heat-treatment to substantially improve the corrosion resistance of non-consumable electrodes, current collectors and other metallic articles employed in electrochemical cells and, at

15   the same time to increase the surface area and to improve the surface texture resulting in substantially enhanced adhesion of surface coatings, including active material and paste adhesion.

       It is a further object of this invention to provide a method for treating at least part of the outer surface of the current collectors made by any of the commercial processes used including

20   gravity casting of "bookmold" or "tubular" grids and by using the "Con Roll" process (Wirtz Manufacturing Inc., Port Huron, Mi, USA) to increase the surface area and improve paste adhesion.

       It is a further objective of this invention to provide a process capable of improving the

25   corrosion properties of the surface and near-surface layer of metallic parts for use in electrochemical cells and not to necessarily impart uniform physical and chemical properties throughout the part. This will be obvious to anyone skilled in the art as the chemical attack in electrochemical cells mostly occurs on or near the surface of the part, which is exposed to typically corrosive electrolytes.

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5   It is another object of this invention that the thermo-mechanical treatment employed to treat the lead or lead alloy current collectors or their precursors substantially increases the percentage of special grain boundaries to increase at least one of the resistance of the lead or lead alloy to creep and resistance to intergranular corrosion and intergranular cracking, wherein the lead or lead alloy has been subjected to at least one processing cycle comprising: suitably

10   deforming the lead alloy below the solvus temperature, and subsequently annealing the lead alloy for a time and temperature sufficient to effect recrystallization to substantially increase the concentration of special grain boundaries.

15   BASIS OF THE INVENTION

        As is known by artisans skilled in the metallurgical art, deformation involves mechanical deformation on an article at a low enough temperature that dislocations are retained, leading to a structure of non-recrystallized, deformed grains. This invention relies on deforming at least part

20   of the surface layer of the article or the entire article below the solvus temperature, preferably between about 40 °C and the solvus temperature, followed by an annealing treatment. Suitable deformation treatments comprise rolling, extruding, punching, expanding, repeated bending or peening.

25   Any of these deformation treatments can be used to induce work into the material. Until now it was reported that the deformation was required to be a cold work step carried out at room temperature or below, as in the Lehockey US Patent. It has now been found that higher temperatures during the deformation can yield improved results, when combined with a suitable recrystallization treatment. The deformation treatment temperature e.g. as determined by the

30   temperature of the strip exiting the rolling mills or extrusion chamber, can be between 25°C and 250°C, more preferably between 35°C and 200°C, 40°C to 150°C and 60°C to 125°C. The maximum deformation temperature needs to be below the solvus temperature of the alloy being treated.

5   The billet or thick strip generally ranges from about 0.030" (0.76mm) to 1" (25.4mm). The rolling process can be carried out by any of the conventionally known techniques, e.g. using equipment provided by Continuus S.p.A. of Milan, Italy. The thickness of the strip can be adjusted to meet the particular battery application, typically the thickness ranges from 0.002" (0.05mm) to 0.125" (3.2mm) inches. Small, e.g. cylindrical thin film type batteries may utilize

10   the foil treated according to this invention in a thickness range of about 0.002" (0.05mm) to 0.010" (0.25mm); automotive 12 to 42V batteries typically use strip thickness ranges of 0.010" (0.25mm) to 0.045" (1.14mm) and industrial battery the strip thickness can reach 0.150" (3.8mm). It is obvious from comparing the strip thickness before and after rolling that significant mechanical work is induced into the strip during the deformation treatment.

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The deformation treatment required prior to the recrystallization step is performed at temperatures ranging from above room temperature (15°C to 25°C) up to the solvus temperature of the material. More typically, the deformation treatment is carried out between 30°C and 125°C, and even more typically between 40°C and 95°C. The thickness reduction ratios can be suitably

20   chosen to deform e.g. a billet to the desired strip thickness and the deformation temperature is adjusted to optimize the creation of special grain boundaries in the subsequent recrystallization heat-treatment.

In this specification, including the claims: a reference to lead means either pure lead or a

25   lead alloy; a reference to deformation means any forming operation such as rolling, extruding, punching, expanding, bending and peening etc. conducted at between ambient temperature and the solvus temperature of the lead or lead alloy; a reference to lead alloy denotes lead that includes one or more specific alloying elements alloyed with the lead.

30   Preferably, the steps of deforming the lead alloy and annealing to recrystallize the lead alloy are repeated a plurality of times. Excessive strain between recrystallization steps can have a negative effect on the present process. However, for lead alloys, unlike other metals, the inventors have found that, at least for some alloys, an improved concentration of special grain boundaries can be obtained with a single step of deforming or straining and annealing.

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The lead alloys may be comprised of at least one alloying element selected from the group comprising, of Ag, Al, As, Ba, Bi, Ca, Cd, Cu, Fe, Li, Mg, Na, Se, Sb, Sn, Sr, and Zn, but the alloy can also include two or more alloying elements. The alloying element(s) need not be soluble in lead. In the case of substantial alloys, the lead alloy is preferably reduced in thickness

10   or strained by approximately 1%-99% in each deformation step, and the lead alloy is then recrystallized, in the annealing step, at a temperature and time sufficient to allow recrystallization to occur, generally in the range of approximately 100° to 325°C (which is below the melting point of the lead or lead-alloys) for 1 second to 360 minutes (preferably from 5 seconds to 360 minutes) and subsequently air-cooled or quenched to ambient temperature. It is to be appreciated that the

15   exact deformation and annealing temperature and time required for recrystallization and the formation of special grain boundaries will vary depending on the alloying additions and the percentages added.

Preferably, in the processed lead and lead alloys, the percentage of special grain

20   boundaries is at least 50% of the total grain boundaries; however, it was found that at least 20%, 30% or 40% of special grain boundaries already improve the corrosion performance.

In accordance with another aspect of the present invention, the lead or lead alloy is subsequently processed into components for lead-acid batteries, for example positive grids or foils

25   and cell interconnects. It is preferred for the lead or lead alloy to be subject, first, to processing according to the present invention, and that this processing be applied to at least a portion of the lead article. The degree of uniformity may depend on the method of deforming the lead alloy, e.g. stamping, extrusion, rolling, expanding, forging, peening, etc., and component geometry.

30   The thermomechanical treatment process according to this invention is different from the prior art approaches which require precipitation or age hardening. Therefore, unlike prior-art precipitation processes, the process described herein is applicable to pure lead and lead-alloys which do not contain the required precipitate formers of the prior art. The process described in this invention enhances the corrosion resistance of lead or lead-alloys regardless of whether the

5   lead alloy contains an alloying material which is precipitated during the deformation step or steps of a precipitation hardening procedure. The process of this invention elevates the contents of special grain boundaries without hardening of the starting lead or lead alloy material. The avoidance of hardening is completely different from the alloys subjected to prior art processes since the prior art processes are specifically directed toward increasing the hardness of the alloy to

10   improve various physical characteristics.

DESCRIPTION OF THE DRAWINGS

15   For a better understanding of the present invention and to show more clearly how it may be carried into effect, reference will be made by way of example, to the accompanying drawings in which:

        Figure 1 is a sectional view through a conventional lead acid battery.

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        Figure 2 is a graph showing variation of cycle life with a critical electrode dimension;

        Figure 3 is a graph showing a comparison of the creep rate for pure as cast lead and the creep rate of pure lead processed by the method of the present invention;

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        Figure 4 is a map of special grain boundary character distribution in (a) cast pure lead and (b) processed method of the present invention.

        Figure 5 is a bar graph summarizing the increases in special grain boundary content for a

30   range of lead-alloy compositions achieved using the method of the present invention;

        Figures 6A and 6B are bar graphs summarizing the improvements in corrosion and electrode growth for a range of lead-alloy compositions achieved using the method of the present invention;

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Figures 7A and 7B are bar graphs summarizing the relative corrosion and electrode growth performance for a Pb-0.03Ca-0.7Sn-0.06Ag alloy in the cast, wrought, and wrought and recrystallized condition; the latter achieved using the method of the present invention.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention relates to the processing of lead and lead alloys for application as positive current collectors and connectors in lead-acid batteries in order to provide superior
15   resistance to creep deformation (growth) and intergranular corrosion and cracking in the batteries acidic environment.

Referring firstly to figure 1, a traditional lead-acid battery, shown generally at 10, comprises a housing 12, an internal compartment 14, electrodes 16, a busbar 18 and electrolyte
20   solution 20. Compartment 14 serves to contain the electrolyte solution 20. Electrodes 16 and busbar 18 have traditionally been made of either a cast or wrought lead alloy. Alloys have traditionally been used, as opposed to pure lead, since appropriate alloying elements are required to provide improved strength, creep resistance and improved gassing characteristics, for example. While traditional lead-acid batteries have proven to be dependable, they have a limited life span
25   and energy density. The life span is due to the creep (growth), corrosion and cracking of the electrodes resulting from successive charge-discharge cycles.

Commercially produced lead-acid battery components are generally formed initially from cast lead or lead alloys. Although deformation is also frequently applied in the rolling of cast
30   ingots or strip to sheet, and then subsequently by slitting and straining the lead alloy sheets to form grids, treatments that result in complete recrystalization of the microstructure have not been used in prior lead-acid battery components. The percentage of special or coincident site lattice (CSL) grain boundaries in as-cast or wrought lead-based lead-acid battery components is always less than 20% and usually in the range of between 14% and 17%. Traditional as- cast and

5   wrought lead-based positive current collectors are susceptible to intergranular corrosion, cracking and creep deformation (growth).

In the present invention, the lead alloy positive current collector components of the battery are provided with a metallurgical microstructure having a high percentage, that is over 20%, 30%,

10   40% or 50%, of special grain boundaries.   Special grain boundaries can be defined crystallographically as lying within

$$\Delta\theta \leq 15°\Sigma^{-1/2} \qquad (1)$$

15   (D.G. Brandon: Acta. Metallurgica. Vol 14, Page 1479, 1966)

of specific coincident site lattice misorientations having $\Sigma \leq 29$. In this specification, including the claims, the term 'special grain boundaries' defines grain boundaries having $\Sigma \leq 29$ and complying with equation 1.

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The method of the present invention comprises processing the lead-based positive current collector components to improve the concentration of special grain boundaries.   More particularly, this is achieved without invoking conventional strengthening mechanisms, such as precipitation hardening, and without substantially altering the tensile strength or hardness of the

25   material.   The process is referred to as Grain Boundary Engineering (GBE).   It has been discovered that lead-based positive current collector components having concentrations of special grain boundaries greater than 20%, preferably greater than 50%, show markedly improved resistance to creep deformation and intergranular corrosion.   As a result, lead-acid batteries having grain boundary engineered lead-based positive current collector components will have

30   improved life spans. Furthermore, as a result of reduced material allowances for degradation by creep and intergranular attack, it is possible to reduce the thickness of the electrodes, and thereby increase the energy density of the batteries.

5   Palumbo et. al.in Grain Boundary Design and Control for Intergranular Stress Corrosion Resistance , Scripta Metallurgica et Materialia, 25, 1775, (1991) and Lehockey et al. in On the Relationship Between Grain Boundary Character Distribution and Intergranular Corrosion in Proceedings of Microscopy and Microanalysis 1996 (G.W. Bailey et al. eds.) San Francisco Press Inc. (1996), p.346, have proposed generic models for intergranular corrosion and cracking,

10   respectively. The contents of these articles are hereby incorporated by reference. However, these articles solely propose theoretical models and do not suggest any applicability to lead, and more particularly, like other known art, contain no direction as to how to increase the concentration of special grain boundaries. The present inventors have now discovered that these models can be used in the design of lighter weight and more compact lead-acid batteries, on the basis that the

15   frequency of special grain boundaries in a lead-acid battery governs its susceptibility to cracking (and loss of electrical continuity) and corrosion (loss of minimum wall thickness) and can be shown to be directly related to overall battery cycle life.

In quantifying the effect of grain size and 'special' grain boundary (i.e., $\Sigma \leq 29$) frequency

20   on bulk intergranular cracking susceptibility it can be considered that a crack initiating at the surface of, and propagating intergranularly into, the electrode, will arrest at a triple junction when both of the available intergranular paths for crack continuation are inaccessible owing to either (1) intrinsic resistance to cracking (e.g., low Σ CSL special grain boundary) or (2) unfavourable orientation to the applied stress axis. The probability (P) of arresting a crack is given by,

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$$P = f_{sp}^2 + 2[f_o f_{sp}(1-f_{sp})] \quad (2)$$

where f_o is the fraction of interfaces in the material which are unfavourably oriented to the applied stress axis (note that f_o is strongly dependent on the grain shape and has a value of 1/3 for

30   conventional equiaxed materials) and f_{sp} is the fraction of special interfaces which are intrinsically resistant to cracking. The probability χ of arresting a crack within a length L from the initiating surface is given by,

$$(1-\chi) = (1-P)^{2L/d} \quad (3)$$

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where d is the average grain size. The probability of crack arrest can be increased by three fundamental approaches:

(1)   increasing the frequency of intrinsically resistant grain boundaries (f_{sp}),

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(2)   decreasing grain size (d), and

(3)   modifying grain shape (f_o).

Intergranular corrosion can also compromise the integrity of a positive lead acid electrode by general loss of cross-sectional thickness arising from "grain dropping'. For any grain to be

15   ejected from the matrix, *all* of its bounding grain boundaries must be fully compromised by corrosion. Assuming that 'special' grain boundaries are immune to corrosion, and considering a material comprised of hexagonal prism grains, it can be shown that the probability of arresting such a grain dropping process at any junction is given by,

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$$(1-P) = (1-f_{sp})^3(1-f_{sp}^3)   \quad (4)$$

The probability (P) derived in eqn (4) can be applied with eqn (3), where it can be shown that, in a manner similar to intergranular cracking, decreasing grain size (d) and increasing special boundary frequency (f_{sp}) are expected to significantly increase resistance to section loss by

25   intergranular corrosion. The operating life of a lead acid battery can be considered to be inversely proportional to the probability of through-wall penetration at the minimum electrode dimension (D_{crit}), by either an intergranular - corrosion or cracking mechanism. From eqns. 2, 3 and 4, and considering that intergranular degradation propagates simultaneously from the two surfaces bounding the minimum dimension (i.e., $D_{crit}=2L$), the

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following expression 5 can be derived for determining the effect of microstructure (i.e., grain size and grain boundary character distribution) on the minimum electrode section thickness required to obtain a given cycle life (C).

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$$D_{crit} = \frac{d * \ln(1-x) * C}{K * \ln(1-P)} \qquad (5)$$

10   In this equation, X is the statistical certainty, and P is the probability of arresting the degradation process, which is obtained from eqn. (3) or eqn. (4) for intergranular -cracking and - corrosion processes, respectively. K is a constant which can be estimated from the typical performance of conventional lead-acid batteries. For example, in severe laboratory testing of typical SLI batteries, a charge- discharge cycle life, C, of approximately 200 is observed with

15   grids having a minimum cross-section of approximately 1mm, average grain size, d, of 50μm, and a microstructure consisting of approximately 15% special grain boundaries (f_{sp}). Assuming a statistical certainty (X) of 99%, these conditions lead to K values of 408 cycles, and 48 cycles for intergranular cracking and corrosion processes, respectively.

20   Figure 2 summarizes the estimated improvements in lead-acid battery performance from increases in special grain boundary content as calculated from eqn (5) for material having a conventional grain size of 50μm. As shown in this figure, significant improvements in cycle life are expected for both intergranular-cracking and corrosion dominated degradation processes, by increasing the population of special grain boundaries, f_{sp}. At conventional SLI positive current

25   collector dimensions of 1mm, increasing the special grain boundary population from that typically observed (i.e., 15%) to 50% is expected to result in approximately a 4 - fold improvement in cycle life. Moreover, as shown in Fig.2, this improvement in performance would allow the use of grids having a minimum dimension of as low as 0.2mm, while still retaining the current performance of SLI batteries. Such a reduction in positive grid thickness would be expected to significantly

30   reduce the size and weight of lead-acid batteries (1mm positive grid accounts for 25% of total battery weight), or result in commensurate increases in energy density.

        Through increasing the special grain boundary fraction in the metal, grain boundary engineering increases the resistance of the metal to crack propagation and strain deformation

35   (creep) by altering the crystallographic structure of the grain boundaries. This is in contrast to previous efforts at providing improved components for lead-acid batteries, such as precipitation or

5   age hardening, which were directed at changing the composition, size and distribution of the microconstituents within the grains. Through a carefully controlled process of deformation and recrystallization, the special grain boundary fraction can be beneficially increased.

The method of the present invention is based on the discovery that the special grain
10   boundary fraction can be increased through careful selection of process parameters for deforming and then recrystallizing the lead or lead alloy. The specified steps may be repeated until the desired concentration of special grain boundaries is achieved. The deformation can take the form of drawing, stamping, rolling, pressing, extruding, expanding, forging, bending or any other physical deformation. We have found that, for lead and some lead alloys, special grain boundary
15   concentrations or fractions of greater than 40% to 50% can be achieved with only one deformation and recrystallization step; however, additional deformation and recrystallization steps may yield a more uniform product having a smaller overall average grain size. A smaller grain size increases the amount of special grain boundaries and thereby improves crack resistance.

20   Furthermore, as described above and as predicted from equation (5), decreasing the grain size beneficially reduces the required level of special grain boundary fraction necessary to show improved results through the present invention. Physical limitations on minimum grain size, though, generally dictate that special fractions of 50% or higher are required to receive improved characteristics with the present invention. It has now been surprisingly found that f_{sp} >20, >30
25   and >40% results in a noticeable improvements of the corrosion performance as well.

It has been discovered that there is a relationship between the recrystallization temperature, the amount of deformation per step, the temperature at which such deformation occurs, the amount of time at which the lead or lead alloy is held at the recrystallization
30   temperature, the composition of the lead or lead alloy used and the resulting special grain boundary fraction in the lead or lead alloy.

The temperature at which the lead is recrystallized is critical to the present invention. Typically, recrystallization will occur in a metal at temperatures over 0.5 Tm, where Tm is the

5 absolute melting temperature in degrees Kelvin. For pure lead, ambient temperature is approximately 0.5 Tm . In the present invention, the temperature at which recrystallization occurs must be chosen so that the special grain boundary fraction is maximized. The temperature must not be so high, however, that excessive grain growth occurs. Moreover, the desired recrystallization temperature must be achieved within a relatively short period of time in order to

10 prevent premature recovery, and in certain alloys, precipitation of secondary phases during prolonged heat-up, which can excessively harden the alloy and hinder the nucleation of new grains and grain boundaries.

Since small changes in the composition of the lead alloy can affect the recrystallization

15 temperature and time required to optimize the special grain boundary concentration in the lead, trial and analysis must be used to determine the amount of deformation, annealing temperature and time, and the number of processing cycles which will maximize the special grain boundary fraction in a given composition of lead.

20 For commercially pure lead, special grain boundary concentrations of greater than 50% can be produced in one or more cycles comprised of induced deformations or strains in the range between 1% to 70% per step, and recrystallization at temperatures within the range of 150°C to 325°C for annealing times in the range of 5 seconds to 360 minutes.

25 For other lead alloys, we have discovered that these can be categorized as Pb-X-Y alloys, where X elements are comprised of the strong precipitate formers and Y elements are the weak or non-precipitating elements. The X elements are comprised of the Group I and Group II elements of the periodic table, which in terms of common and potential battery alloying constituents include: Li, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Ba, and Sb. The Y elements are comprised of

30 other common lead alloying constituents which include: Ag, Sn, Cu, Zn, As, and Bi.

Certain combinations of alloying elements result in the formation of better strengthening precipitates then when present alone. This applies to Sn if it is in the presence of Ca as this forms the very effective strengthening precipitate, $CaSn_3$. In most cases, sufficient Sn is added to result

5   in an excess for electrochemical reasons. In this case the element might also act as a solid solution or as a second phase hardener.

For lead alloys where the cumulative concentration of X elements is less than 0.05 wt.%, and the cumulative concentration of Y elements is in the range of 0.5 to 5 wt.%, hereafter referred

10   to as Class I alloys, then a single cycle of deformation or strain between 10% and 40% and recrystallization at a temperature between 200 °C and 280 °C for a time in the range of 10 seconds to 10 minutes, followed by air cooling to ambient temperature, will yield a microstructure consisting of a special grain boundary content of greater than 50%.

15   For lead alloys where the cumulative concentration of X elements is greater than or equal to 0.05 wt.%, and the cumulative concentration of Y elements is in the range of 0.5 to 5 wt.%, hereafter referred to as Class II alloys, then two or more cycles of deformation or strain between 40% and 80% and recrystallization at a temperature between 200 ° and 280 °C for a time in the range of 10 seconds to 10 minutes, followed by air cooling to ambient temperature, will yield a

20   microstructure consisting of a special grain boundary content of greater than 50%.

The treatment time varies, depending on the material, but typically ranges from 1 seconds to three days, more typically from 5 seconds to 12 hours, and preferably from 10 seconds to 3 hours.

25

In all cases, the specific recrystallization temperature and time must be optimized to achieve complete recrystallization. In cases where rapid heat-up rates are obtainable such as is achievable in salt baths and fluidized bed furnaces, annealing times can be reduced significantly.

30   The method of the present invention will now be illustrated by way of the following examples.

EXAMPLE #1

5

Strips of commercially pure lead, in an as cast condition, were subjected to six cycles each comprising a deformation step and a recrystallization step. The deformations were performed on a rolling mill at room temperature and were limited to 20% reduction in thickness per step. Each recrystallization treatment was carried out at 160°C for 15 minutes.

10

Each sample of grain boundary engineered material and control was analyzed to determine the percentage of special grain boundaries. The results are summarised in Table 1, at the end of the description. As can be seen from Table 1, for pure lead, the concentration of special grain boundaries in the as cast material was 16.5%. The concentration of special grain boundaries in

15   the grain boundary engineered material was 64.7%. Clearly, the processing method dramatically increases the number of special grain boundaries. The microstructures of the cast and GBE-processed materials are depicted in Figure 4.

To measure the samples resistance to strain deformation, which is directly related to

20   positive current collector growth in a lead-acid battery, standard ASTM E139 creep tests were performed. Each sample was subjected to a strain of 4.8 MPa over a period of several hours at room temperature. The amount of deformation, in millimetres, was then plotted as a function of time. The results are summarised in Figure 3. The rate of strain deformation over time for the as cast material was calculated as 1150% per year. By comparison, the rate of strain deformation

25   for the grain boundary engineered material was found to be only 35% per year. The grain boundary engineered material processed by the embodiments of the present invention showed greatly increased resistance to strain deformation. It should be noted that this result cannot be attributed to precipitation effects as outlined in the work of Tilman and Myers as the commercially pure lead does not contain any precipitate forming elements, and further

30   underscores the novelty of this present invention.

Table 1: Relative percentage of special grain boundaries in commercially pure Pb.

	As Cast [%]	GBE [%]
Random(Σ>29)	83.5	35.3
Special ($\Sigma\leq$29)	16.5	64.7

EXAMPLE #2.

A series of commercial lead alloys of the Class II type previously described, were obtained in a conventional cast condition in the form of strip. These strips were subsequently processed using the techniques described in the present invention. The specific alloys and processing conditions are summarized as follows.

A Pb-0.073wt% Ca-0.07wt% Sn alloy (Class II) was processed by three cycles each comprised of cold rolling at room temperature to achieve a 40% reduction in thickness, annealing at 270 °C for 10 minutes in air followed by air cooling. The resulting microstructural improvement in terms of special grain boundary content is summarized in Figure 5 (identified as PbCaSn in Figure 5). The special grain boundary content was increased from 11% in the as-cast starting material, to 51% in the material processed by the method described.

A Pb-0.065wt% Ca-0.07wt% Sn 0.03wt% Ag alloy (Class II) was processed by two cycles each comprised of cold rolling at room temperature to achieve a 40% reduction in thickness, annealing at 250 °C for 10 minutes in air followed by air cooling. The resulting microstructural improvement in terms of special grain boundary content is summarized in Figure 5 (identified as PbCaSnAg in Figure 5). The special grain boundary content was increased from 12% in the as-cast starting material, to 70% in the material processed by the method described.

A Pb-0.073wt% Ca-1.4wt% Sn alloy (Class II) was processed by two cycles each comprised of cold rolling at room temperature to achieve a 40% reduction in thickness; annealing at 250 °C for 10 minutes in air followed by air cooling. The resulting microstructural improvement in terms of special grain boundary content is summarized in Figure 5 (identified as PbCa"Hi"Sn in Figure 5). The special grain boundary content was increased from 17% in the as-cast starting material, to 70% in the material processed by the method described.

5

The performance of these alloys in both the as-cast and GBE-processed conditions as described above were evaluated in industry standard tests whereby grids of 0.59mm thickness were formed from the strip materials. Corrosion tests were conducted by static polarization in a solution of 1.27 specific gravity sulfuric acid at 70 °C and polarized at an overpotential of 200

10   mV for 20 days. Grid electrodes were weighed to the nearest milligram prior to and following exposure to the solution to establish mass loss due to corrosion. Cycling tests were conducted with pasted grids assembled into individual battery cells. Grid weights to the nearest milligram were established prior to pasting. Positive grids were cycled between 0.8 V and 1.4V at a rate of two cycles per day for 35 days in a solution of 1.27 specific gravity sulfuric acid at 70 °C. Upon

15   completion of the test, grids were cleaned of residual paste, and reweighed to the nearest milligram. Also, grid growth susceptibility was established by digitally scanning the area of the grids both prior to and following the test exposure.

The performance of the processed Class II alloys (GBE) relative to their conventional cast

20   counterparts are summarized in Figures 6A and 6B. In all cases, the alloys processed according to the present invention displayed significantly reduced corrosion and growth rates relative to their cast counterparts.

25   EXAMPLE #3

A Pb-0.03 wt %Ca-0.7 wt.% Sn 0.06wt%Ag alloy, representative of a Class I alloy was produced using a commercial rotary net shape casting process. The cast strip of 0.86-0.89 mm thickness was subsequently subjected to a single processing cycle comprised of approximately

30   20% cold tensile strain (room temperature), and heat treatment in an air convection oven at a temperature of 250 °C for 5 minutes followed by cooling to ambient temperature. The strain was introduced at room temperature solely through the grid expansion process and was controlled by the tool die geometry (i.e., diamond height of expanded mesh). For comparison purposes a wrought strip was produced without subsequent recrystallization heat treatment. In this case, cast

5   strip of 1.72mm thickness was cold rolled by 50% and similarly expanded to mesh. The proportion of special grain boundaries present in the as-cast, wrought, and single step GBE processed materials were found to be 16.0%, 15.4% and 64.4%, respectively.

The relative corrosion and growth performance of these materials was evaluated in cycling

10   tests as described in Example 2 at a higher temperature of 75 °C for 20 days. The results are summarized in Figures 7A and 7B which shows that the material processed according to the present invention displays significantly reduced corrosion susceptibility, particularly with reference to the wrought material. In terms of growth, the GBE material significantly outperforms both its cast and wrought counterparts.

15

EXAMPLE #4

Various lead alloys were subjected to the deformation and annealing cycle used to make

20   the recrystallized lead-alloy according to this invention. Each of the samples was deformed at room temperature to 25% reduction in thickness and then annealed by heat-treating at 255°C for five minutes. After the deformation reduction and annealing, each of the aforementioned lead alloys was tested for hardness. A minimum of six hardness measurements at each of two locations of the test alloys were obtained using a Shimadzu model HMV2000 micro hardness

25   tester utilizing a 25g load. The hardness of each metal was also measured in the same way in the as-cast condition (i.e. without being subjected to deformation and annealing cycle). The f_{sp} count of the as-cast material samples prior to GBE processing in all cases was between 10 and 15%. The results of the hardness test for each of the lead alloys is shown in Table 2. In all instances, the deformation reduction and heat annealing cycle resulted in an alloy having a lower hardness

30   than the one of the corresponding as-cast alloy.

Table 2: Hardness of common age-hardenable lead alloys immediately after casting and after GBE processing.

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Alloy Composition	As cast hardness [Vickers Hardness]	GBE Processed		
		Hardness Vicker's DPH	f_{sp} (%)	Grain Size (μm)
Pb-0.05Ca-1.5Sn-0.06Ag	13.4$\pm$0.5	9.9$\pm$0.4	68	18
Pb-0.08Ca-1.25Sn	20.8$\pm$0.6	13.0$\pm$0.6	68	18
Pb-0.065Ca-0.7Sn-0.03Ag	15.5$\pm$1.5	8.5$\pm$0.6	74	58
Pb-0.02Ca-1.0Sn-0.04Ag	13.5$\pm$0.3	7.4$\pm$0.2	66	128
Pb-0.02Ca-1.0Sn-0.04Ag-0.05As	8.3$\pm$0.2	7.0$\pm$0.2	56	26
Pb-0.02Ca-1.0Sn-0.04Ag-0.05Zn	9.2$\pm$0.3	7.4$\pm$0.1	64	97
Pb-0.016Ca-0.77Sn-0.06Ag	11.2$\pm$0.8	8.6$\pm$0.5	67	58

EXAMPLE #5

An age hardenable alloy (Pb-2.0Sb-0.15As) was cast (Vickers hardness after casting: DPH=11) subjected to three cold-working/annealing cycles of the present invention, wherein each cycle comprised a 20% cold rolling step at room temperature followed by a heat treatment annealing step at 180 °C for five minutes. The f_{sp} increased from 10% (as cast) to 59% (after subjecting the sample to the GBE processing). For comparison, one set of samples was processed according to Meyers (US 4,753,688), more particularly, to nine sequential cold rolling cycles of 25% (without intermittent annealing) followed by a final heat treatment at 230 °C for one minute.

The hardness of the age hardenable lead alloy was measured immediately after completion of the respective treatments and at various times of aging at room temperature. The same hardness measurement technique described in example 4 above but using a 50 gram load was used. The hardness numbers are depicted in Table 3. The results clearly indicate that the Meyers process results in an as-processed hardness (VHN: 12) which is greater than that of the as-cast material (VHN:11), and significantly higher than that of the GBE-processed material (VHN: 8) It also shows significantly enhanced short term hardenability whereby its hardness increases to VHN:21 within the first 24 hours of aging. In comparison, the GBE material shows no increase from its initial value during the same time frame. Over a further ten-day period of aging (240 hours) the Meyers-processed material shows a further hardness increase to 27 VHN. It is also

5   noted that the GBE processed material even after 240 hours has a hardness which is not as great
as the as-cast hardness.

10   Table 3: Hardness as a function of aging time at room temperature for Pb-2Sb-0.15As processed
according to Meyers and according to this invention.

Aging time [hours]	Meyers process [Vickers Hardness]	GBE Processed [Vickers Hardness]
0	12	8
24	21	8
240	27	9.5

EXAMPLE #6:

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Various lead alloys were subjected to the GBE processing of the present invention. In the
case of the Pb-1.8Sb-1.05Sn-0.17As alloy the treatment represented two successive cycles of a
50% thickness reduction at room temperature followed by an annealing treatment of 3 minutes at
220 °C. In the case of the Pb-0.08Ca-0.3Sn alloy the treatment represented a 30% thickness

20   reduction at room temperature followed by an annealing treatment of 10 minutes at 300 °C,
followed by three successive cycles of a 40% thickness reduction at room temperature followed
by an annealing treatment of 10 minutes at 290 °C. In the case of the Pb-0.04Ca-0.65Sn-0.03Ag
alloy the treatment represented a 60% thickness reduction at room temperature followed by an
annealing treatment of 3 minutes at 250 °C. In the case of the Pb-0.07Ca-1.4Sn alloy the

25   treatment represented three successive cycles of a 50% thickness reduction at room temperature
followed by an annealing treatment of 10 minutes at 270 °C.

The ultimate hardness of each of the metals was measured after four weeks of age
hardening. The hardness values were obtained using the measurement described above with a 50

30   gram load. The hardness of each alloy prior to GBE processing (i.e., the as cast hardness) was
also measured using the same technique as was used to measure the GBE processed hardness.
The obtained hardness values for each of the alloys processed according to this invention and as

cast are shown in Table 4, as is the f_{sp} count and grain size for the GBE processed samples. The as-cast samples ranged in f_{sp} count from 10 to 15%. Table 4 established that the ultimate hardness achievable by age hardening of the GBE processed materials is not as great as the as-cast hardness demonstrating that GBE-processed materials permanently possess hardness values equivalent to or less than that of the as-cast counterparts.

Table 4: Ultimate hardness values achievable by room temperature aging of as-cast and GBE processed lead-alloys

Alloy Composition	As cast hardness [Vickers Hardness]	GBE Processed		
		Vickers hardness	f_{sp} (%)	Grain Size(um)
Pb-1.8Sb-1.05Sn-0.17As	17.0	15.5	63	15
Pb-0.08Ca-0.3Sn	14.2	10.6	63	18
Pb-0.04Ca-0.65Sn-0.03Ag	14.5	10.5	57	49
Pb-0.07Ca-1.4Sn	19.5	10.5	68	18

EXAMPLE #7:

A Pb-0.06Ca-1.2Sn alloy was cast and processed using rolling deformation at various temperatures as indicated in the table 5. As is evident from the data, working the strip at temperatures of 20, 40 and 80 °C, followed by an annealing treatment, raised the f_{sp} count of the samples to over 60% in all cases and lowered the UTS to a value below the one of the as cast or room temperature rolled sample.

Table 5: Rolling temperature vs f_{sp} and UTS for various processing parameters.

	Rolling Conditions	Annealing Condition	f_{sp} (%)	UTS (MPa after 7 days)
g	N/A (as cast)	N/A	14	46.8
h	20 °C (RT= Room Temp), reduced from 7mm to 1mm	N/A	N/A (not recrystallized)	51.0
a	20 °C (RT), reduced from 7mm to 1mm	GBE(280 °C/5 min)	62	30.0
b	40 °C, reduced from 7mm to 1mm	GBE(280 °C/5 min)	62	32.0
c	80 °C, reduced from 7mm to 1mm	GBE(280 °C/5 min)	76	34.5

EXAMPLE #8:

A Pb-0.06Ca-1.2Sn alloy was processed using hot deformation with and without a subsequent annealing treatment as indicated in Table 6. The fsp count of hot deformed Pb-alloys using rolling or extrusion elevated the fsp count to over 40% even without a subsequent annealing step.

Table 6: Rolling temperature versus fsp and UTS for various processing parameters.

	Rolling Conditions	Annealing Condition	f_{sp} (%)
h	20 °C (RT= Room Temp), reduced from 7mm to 1mm	N/A	N/A (not recrystallized)
d	200 °C (rolled right after casting below the solvus temperature), reduced from 12.5mm to 5mm	N/A	43
e	200 °C (rolled right after casting above solvus), reduced from 12.5mm to 5mm	GBE(280 °C/5 min)	50

Similar results were achieved when the strip was extruded at temperatures ranging from

5   50 °C to 200 °C or below the solvus temperature of the Pb-alloy.

EXAMPLE #9:

10   30 cm long sections were cut from a 10cm wide rolled lead alloy strip, containing 0.065%

Ca, 1.2% tin and the balance commercial purity lead. One set of samples shot peened, the other

(control) was left untreated. The ASTM D 1876-95 peel test was applied to determine the

adhesion (Table 7). The samples cut to a width of 25mm, cleaned in an ultrasonic bath with

acetone and bent to a 90° angle, 4 to 5 cm from the end that had previously been clamped. To

15   simulate the application of a paste containing active material a film of epoxy (Hysol EPK 608

epoxy) was used. Two samples were bonded together by the epoxy, followed by suitable curing

(24 hours). The samples were tested using the Instron 4201 Universal Tester. The results are

listed in table 7. The T-peel test demonstrated that the peened surface improved uniformity of the

bond strength and cohesion failure was observed with these specimens. The smooth (control)

20   surface specimens exhibited adhesion failure.

Table 7. ASTM D 1876-95 Peel Test of Pb-0.065%Ca-1.2%Sn Sample

	Peel Strength [N]
Control	189
This Invention	>291[*)]

25

*) In this test the epoxy film fractured (cohesion failure) and did not delaminate from the

substrate.

          This test clearly indicates that the shot peened surface results in a substantial improvement

30   (over 50%) in the adhesion.

5   EXAMPLE #10

          A set of Pb-Ca-Sn-alloy bookmould cast grids was surface peened at room temperature for

10 seconds, followed by heat treatment (275 °C, 10 minutes). Careful analysis of grid cross

sections revealed that the penetration depth achieved extended up to 350 micron below the peened

10   surface and that the grain size in the near surface layer was 10 micron, while it remained at about

260 micron in the bulk material. The surface layer of the peened and annealed sample had a of

40%, whereas the untreated sample f_{sp} and the f_{sp} of the treated material more than 350 microns

below the surface remained at 15% (table 8).

f_{sp}

15

5 Table 8: Summary of microstructural characteristics.

	f_{sp} (%)	Grain Size	GBEST Depth
Bulk Material	15%	260µm	-
GBEST Layer	40%	10µm	350µm

EXAMPLE #11:

10

Two Pb-Ca-Sn alloys were cast into sheets. An as received set representing prior art and a set processed according to the invention were corrosion tested in an environment representative of a zinc-electrowinning operation. The peening was performed using 28 mil steel shot at 80 psi at room temperature. Three passes per substrate were performed within three minutes and the

15 peened samples were subsequently annealed at 250 °C for 10 minutes. A pretreatment comprising a 30 minute soak at 300 °C was used to modify existing precipitates to facilitate the GBE process. The following table illustrates the sample characteristics and the corrosion performance.

The corrosion test was performed by submersing test samples in a typical zinc

20 electrowinning electrolyte (160 g/l sulfuric acid, 60 g/l Zn^{++} at 60 °C) and anodizing them at 40 mA/cm2 against steel cathodes. The results are depicted in tables 9 and 10.

Table 9: f_{sp} count and corrosion rates for a cast and peened Pb strip (0.82% Ca, 0.55%Ag, balance

25 commercial purity Pb)

	f_{sp} center [%]	f_{sp} surface (0-200µm) [%]	Corrosion Rate (averaged over 39 days) [mm/yr]	Corrosion Rate (Averaged over 62 days) [mm /yr]
As received	15	15	2.4	2.1
Processed according to this invention	15	45	1.8	1.6

5   Table 10: f_{sp} count and corrosion rates for a cast and peened Pb strip (0.40% Ca, 0.31%Ag, balance commercial purity Pb).

	f_{sp} center [%]	f_{sp} surface (0-200µm) [%]	Corrosion Rate (averaged over 39 days) [mm/yr]	Corrosion Rate (averaged over 62 days) [mm/yr]
As received	15	15	1.8	1.4
Processed according to this invention	15	50	1.6	1.2

10